Nanoparticle Colloids

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Utilizing the Krafft Phenomenon to Generate Ideal Micelle-Free Surfactant-Stabilized Nanoparticle Suspensions**

Sarah Dölle, Bob-Dan Lechner, Ji Hyun Park, Stefan Schymura, Jan P. F. Lagerwall, and Giusy Scalia**

The diverse attractive properties of nanoparticles have triggered considerable efforts devoted to their exploitation in devices and new materials, as well as their academic investigation.[1,2] Often a necessary first step in their handling is the dispersion of the particles in a liquid,[3,4] typically an aqueous surfactant solution.[5] While this step allows efficient individualization, purification and—in the case of single-wall carbon nanotubes (SWCNTs)—fractionation,[2] the method also brings some critical disadvantages. It is very difficult to remove the surfactant after the particles have been deposited on a target substrate or incorporated into a matrix, where it severely decreases the performance of devices[6] or composites,[7] and in suspensions surfactant micelles promote particle aggregation through depletion attraction.[8]

Considering these key roles of surfactants, it is remarkable that the influence of the Krafft temperature T_K—the temperature below which no micelles are formed because the surfactant solubility is below the critical micelle concentration (CMC)[9]—has never been discussed in this context. Herein we show, using SWCNTs as example, that dispersion below T_K yields better exfoliation, higher nanoparticle loading, and dramatically reduced excess surfactant.

We disperse SWCNTs using ultrasonication at 0°C (details in Supporting Information) at loadings ranging from 0.1–1.2 mg mL^{-1} in aqueous solutions of cationic surfactant hexadecyl trimethylammonium bromide (CTAB). CTAB is effective in dispersing CNTs[4] and it is convenient owing to its high $T_K = 25\,°C$. The CTAB concentration is set to 1 wt% (far above $CMC_{CTAB} \approx 0.036$ wt%), a typical choice for CNT dispersion.[10] By cooling to $T < T_K$ we fully suppress micelle formation because only a fraction of surfactant can stay in solution below the CMC. The excess precipitates as crystalline needles. When adding hydrophobic CNT powder the surface of the grains (initially large and containing vast numbers of aggregated nanotubes) is covered by surfactant, temporarily reducing the CTAB concentration to below saturation and thus allowing some of the crystal phase to dissolve. As the grains are successively broken up during sonication the exposed CNT surface increases dramatically, leading to adsorption of new surfactant that thereby leaves solution and makes further dissolution of CTAB crystals possible. This cycle repeats until all the CNTs have been exfoliated, the sample is then either centrifuged or left to stand at $T < T_K$ so that excess surfactant sediments out. By extracting the supernatant we finally achieve a suspension of mainly individually dispersed CNTs at a concentration that can be very high, and that contains no more surfactant than that required for stabilizing the nanoparticles, regardless of their concentration.

The surfactant sediment is light gray (Figure 1), revealing that it also contains some CNT aggregates and/or impurities. It is also apparent that an increase in CNT concentration leads to less sediment. Because the total amount of CTAB is the same in all samples, this shows that an increasing fraction of the surfactant is bound to suspended nanotubes as the concentration of nanotubes is increased. Surfactant from the crystalline phase is thus indeed made available for CNT adsorption during sonication at $T < T_K$. A quantitative analysis of the sediment (see Supporting Information) reveals that the CTAB:CNT mass ratio in the supernatant is about 2:1.

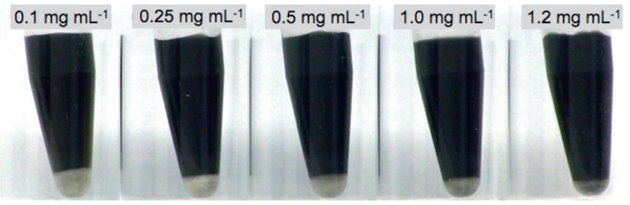

Figure 1. Aqueous 1 wt% CTAB dispersions of SWCNTs (concentrations indicated at the top) prepared at 0°C (that is, below $T_K = 25\,°C$). The samples were left standing for one week at 20°C to ensure complete sedimentation of the insoluble excess surfactant.

As a reference we prepared a series of suspensions identical in composition but differing in the handling temperature, which was set to 30°C, that is, above T_K. All the surfactant thus dissolves, giving micelles. Under the optical

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[*] S. Dölle, B.-D. Lechner, S. Schymura, Prof. J. P. F. Lagerwall
Martin-Luther-University Halle-Wittenberg, Institute of Chemistry
von-Danckelmann-Platz 4, 06120 Halle (Germany)

J. H. Park, Prof. J. P. F. Lagerwall, Prof. G. Scalia
Seoul National University, Graduate School of Convergence Science and Technology and Advanced Institutes of Convergence Technologies, Department of Nano Science and Technology
Suwon-si, Gyeonggi-do, 443-270 (Korea)
E-mail: jan.lagerwall@lcsoftmatter.com
giusy.scalia@solcanta.com
Homepage: http://www.snm.lcsoftmatter.com

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microscope both series reveal some visible aggregates, thus all the samples were centrifuged briefly (the $T < T_K$ samples maintained at 15 °C, the others at 30 °C), removing all optically resolvable aggregates.

To quantify the long-term stability of the samples, the optical absorption of their supernatants was measured after one month of standing at adequate temperature (slightly below and above T_K, respectively), before and after centrifugation. The Lambert-Beer law [Eq. (1)]

$$A = \log\frac{I_0}{I} = \varepsilon c l \qquad (1)$$

correlates the absorbance A with the particle concentration c through the extinction coefficient ε (I_0 and I are light intensity before and after the sample, respectively, and l is the light path length). By fitting Equation (1) to the absorbance data prior to centrifugation, with c set to the initial SWCNT concentration c_0, we can determine an extinction coefficient for $T < T_K$ of $\varepsilon_< = 3.4\ \mathrm{L\,mg^{-1}\,m^{-1}}$ and for $T > T_K$ of $\varepsilon_> = 2.4\ \mathrm{L\,mg^{-1}\,m^{-1}}$ (Figure 2). Well individualized CNTs result in higher effective ε, hence a higher value for $T < T_K$ is a strong indication that preparation and storage below T_K ensures a significantly more stable suspension. In the $T > T_K$ samples ε apparently decreases, this is most likely due to micelle-driven tube bundling. This assumption is corroborated by recent cryo-TEM investigations of CTAB-stabilized SWCNT suspensions prepared at $T > T_K$,[11] revealing aggregation into small islands. Upon centrifugation both series show some absorbance loss, reflecting removal of aggregates.

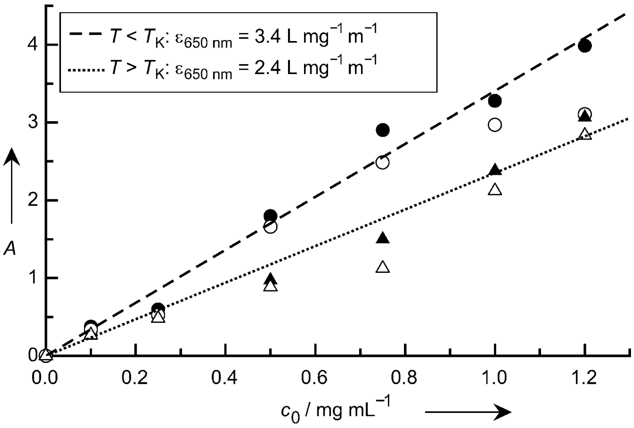

Figure 2. Absorbance A at 650 nm of samples prepared below (circles) and above (triangles) T_K, as a function of initial CNT concentration c_0. Filled and empty symbols show data before and after centrifugation, respectively. Dashed and dotted lines are best fits to the pre-centrifugation data for $T < T_K$ and $T > T_K$, respectively, giving the Lambert-Beer extinction coefficient ε for each series.

Absorption spectra from individually dispersed CNTs feature characteristic oscillations, which gradually disappear if the nanotubes aggregate.[10,12] The absorption spectra of the $T < T_K$ samples show clear oscillations even after the long standing period, the influence of centrifugation being marginal (Figure 3 a,b). These results indicate that very little CNT bundling has taken place, in contrast to the $T > T_K$ case for which the spectra are almost flat even after centrifugation (on magnification, the characteristic oscillations can however still be detected; Figure 3 c,d).

To obtain a nanoscale picture of the dispersion quality we carried out atomic force microscopy (AFM) investigations of the supernatants after centrifugation of the 0.5 and 0.25 mg mL^{-1} samples of each series. This study revealed dramatic differences between the series (Figure 4 and Figure S2 in the Supporting Information). Figure 4 a and d reveal that the $T > T_K$ sample has a smaller number of larger CNT bundles than the $T < T_K$ sample. Zooming in (Figures 4 b and e) shows that the CNT bundles in the $T > T_K$ samples are some tens of nm wide, whereas the bundle width in the $T < T_K$ sample is at the lateral resolution limit of the AFM. Typical bundle heights are about 3–4 nm and 1–2 nm in Figures 4 b and e, respectively. The majority of the tubes dispersed at $T < T_K$ are thus present as individual tubes or bundles of just a few CNTs, while the tubes prepared above T_K are collected in aggregates.

The differences are even more striking in the AFM phase data (Figure 4 c and f). The $T > T_K$ features have a smeared-out appearance and varying brightness, suggesting that they are composed of multiple constituents. The features are clearly not just CNTs, but a composite structure where nanotubes are embedded in substantial amounts of surfactant. The $T < T_K$ sample is different, with sharp-edged elongated objects without internal modulation. These are single tubes or tiny bundles with no sign of surfactant coverage. The AFM study of the more concentrated sample reveals an even greater difference between the two series (see Supporting Information).

The difference in surfactant coverage between the two series is of great practical importance, as only the pristine nanoparticles should remain in a final device's structure, substantial performance reduction or device failure being possible consequences of surplus surfactant. The same holds for nanoparticles in composites, where the surfactant can degrade the overall quality of the composite and diminish the anchoring strength between particles and matrix.

It is reasonable to ask if the better results for $T < T_K$ are solely due to the reduced CTAB concentration in the supernatant or if the dispersion below T_K has a general beneficial effect. As a final comparison, a reference experiment was therefore performed where 1 mg of CNTs was suspended at 30 °C in 1 mL of water containing 2 mg of CTAB, that is, with the same reduced CTAB:CNT ratio as in the supernatant of the $T < T_K$ samples. The results (Supporting Information) reveal that the suspension with this optimized CTAB concentration was still not as good as that prepared below T_K, although the amount of surplus CTAB was naturally lower. We attribute the difference to the fact that micelles are also present at this concentration (> CMC), hence there is an equilibrium throughout the preparation process between surfactant coating the CNTs and surfactant forming micelles. Moreover, dispersion below T_K offers the additional important practical advantage that it automatically ensures optimum surfactant concentration regardless of the concentration of CNTs, their characteristics and the charac-

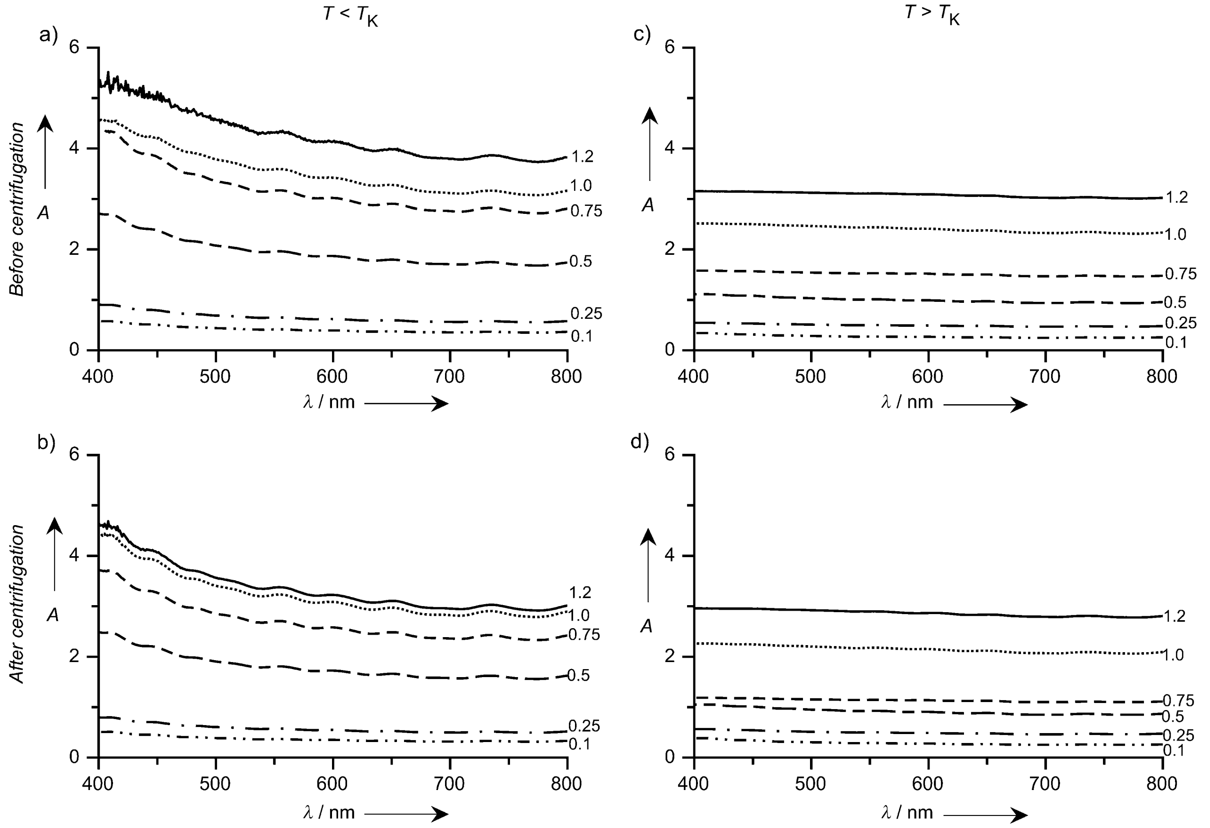

Figure 3. Absorption spectra as a function of wavelength λ of SWCNT suspensions prepared and measured below (left) and above (right) T_K, after one month of standing. The initial CNT concentration in $mg\,mL^{-1}$ is shown to the right of each curve.

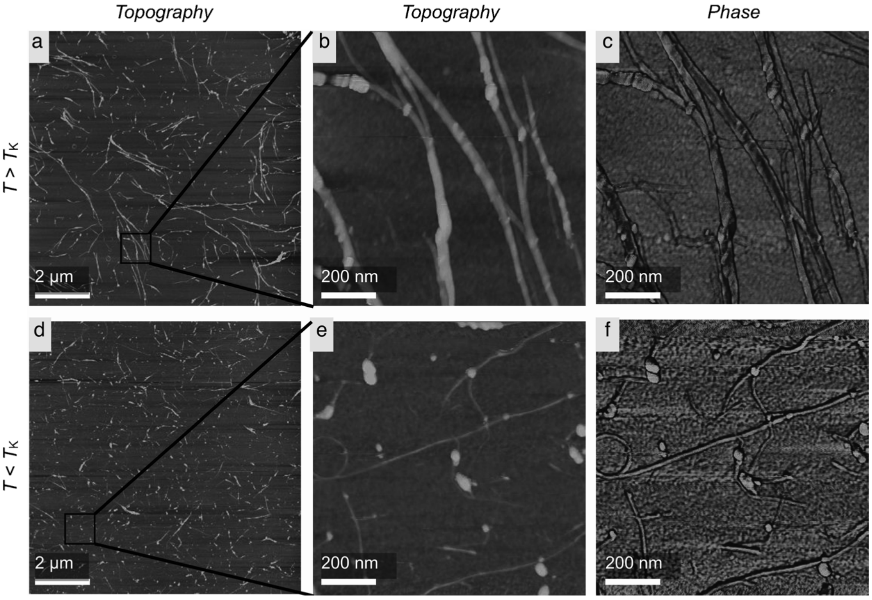

Figure 4. AFM images of samples with an initial CNTs concentration of 0.25 $mg\,mL^{-1}$, prepared at $T > T_K$ (a–c) and $T < T_K$ (d–f).

teristics of the surfactant. The effective specific CNT surface area varies greatly with type (SW- or multiwall (MW-) CNTs), production method, and even between batches, and also the sonication time and intensity will affect it (strong sonication exfoliates bundles efficiently but may damage the tubes, mild treatment is less destructive but leaves some bundles intact). For dispersion above T_K, the optimum surfactant concentration would thus have to be determined for every combination of CNT, surfactant, and dispersion procedure, whereas this is unnecessary if the dispersion is carried out at $T < T_K$.

Our novel approach has been demonstrated using SWCNTs, but the basis is a fundamental physicochemical phenomenon of surfactant-stabilized colloidal dispersions. It is thus applicable to any category of hydrophobic nanoparticles, including for example, pristine (non-oxidized) graphene, giving it broad relevance for today's research and applications in nanotechnology and materials science. For most commonly used ionic surfactants T_K is well above 0 °C, hence the new route is not limited to CTAB. Preliminary results with sodium dodecyl sulfate (SDS; $T_K = 14\,°C$) are promising although the lower T_K makes handling more inconvenient. Sodium dodecyl benzene sulfonate (SDBS) may be ideal since it is very effective for CNT dispersion[13] and its linear single-chain isomer has been reported to have $T_K = 27.6\,°C$.[14] However, commercial SDBS samples contain multiple isomers, leading to a lower T_K.[15] Therefore, no phase separation occurs at practical dispersion conditions when using readily available SDBS. With uni-isomeric SDBS very high-quality suspensions may be expected, benefiting from a very efficient surfactant and the advantages of working below T_K.

Herein we have shown that the dispersion of nanoparticles at temperatures below the Krafft temperature T_K of the surfactant used for stabilizing the suspension is beneficial in many respects. First, it provides an easy means of ensuring an optimum amount of surfactant, irrespective of the concentration and character of the nanoparticles. Second, the suspension contains no micelles, thereby eliminating particle aggregation by depletion attraction. As a consequence, the nanoparticle concentration can be kept as high as the efficiency of the surfactant allows, in contrast to $T > T_K$ suspensions where high nanoparticle concentration suspensions are destabilized by depletion attraction. Third, the long-term stability is dramatically improved as evidenced by optical spectroscopy. Finally, and perhaps most important, the procedure minimizes remaining surfactant after depositing the particles on a target substrate or incorporating them in a composite matrix, much to the benefit of the device or material.

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